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Decomposition of *Juncus* seeds in a valley mire (Faroe Islands) over a 900 year period

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Abstract

The influence of past depositional environments on the chemistry of sub-fossil *Juncus* seed coats (testa) from the top 1 m (corresponding to ca. 900 years of peat accumulation) of a peat bog in the Faroe Islands was examined. The chemistry of the testa of fresh *Juncus* seeds were characterised using thermally assisted pyrolysis and methylation (THM) in the presence of tetramethyl ammonium hydroxide (TMAH) and ‘type’ compounds were identified, representative of the major chemical groups in the testa (cellulose-related sugars, lignin-related phenolics, fatty acids). The abundance of the ‘type’ compounds in the products from sub-fossil testae (the internal tissues of the seeds do not survive beyond the very early stages of decomposition) was then quantified at contiguous 1 cm depth intervals. Major losses of C₁₈ unsaturated fatty acid methyl esters and sugars were associated with the fresh to sub-fossil transition at ca. 7 cm depth. The preservation of the phenolic ferulic acid in the seed testa appears to be favoured by the input of small basaltic particles from the nearby stream channel. The mechanism by which inwash of inorganic material may be responsible for the improved chemical preservation of the *Juncus* seed testa is, however, unclear. The sugars were easily metabolised by microorganisms under aerobic conditions of low water table and preserved under anoxic conditions with high water table, suggesting that a drier mire surface may result in the more efficient depletion of polysaccharides and cellulose during the initial stage of decomposition in the acrotelm.

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1. Introduction

Decomposition is a major process affecting wetland carbon dynamics and so has a role in the global CO₂ cycle and climate change (Maltby and Immirzi,

1993). However, the processes controlling the decomposition of organic matter (OM) in peatlands are not well understood. In particular, changes in the height of the water table may result in fluctuations between aerobic and anaerobic conditions. In the upper aerobic acrotelm, both polysaccharides and lignin are degraded rapidly by white-rot fungi (Kirk and Farrell, 1987; Lewis and Yamamoto,

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1990; Akin et al., 1996; Huang et al., 1998), while in the deeper anaerobic catotelm, bacteria are the decomposers, degrading polysaccharides (Benner et al., 1984; Young and Frazer, 1987; Opsahl and Benner, 1995). It has long been recognised that the plant remains comprising the peat mass are well preserved owing to the slow, inefficient biodegradation in the permanently waterlogged catotelm (Clymo, 1984, 1991).

Long term (>25 y) studies of decomposition in wetlands have tended to focus on chemical analysis of bulk peat samples, with measurement of elements (C, N; e.g. Kuhry and Vitt, 1996) and organic compounds using techniques such as pyrolysis-gas chromatography–mass spectrometry (py-GC–MS; e.g. Kracht and Gleixner, 2000). However, the peat mass may be described as a mixture of plant species and plant parts, each component having a different chemical composition and decomposition rate. The results of long term degradation studies may be more influenced by changes in the botanical composition of the peat than by environmental controls such as variation in water table depth (see Clymo, 1991, pp. 86–90 for a discussion). The variation due to the mixture of taxa can be eliminated if a single species is studied. However, the only studies that have adopted this type of approach is that of van der Heijden and Boon (1994), who examined *Calluna* wood from a raised bog, and Kuder and Krüge (1998) who examined chemical changes in sedge fibres from the top 110 cm of a Polish bog.

In comparison with herbaceous tissue, reproductive structures such as pollen, spores and seeds are often very well preserved in peat deposits. In seeds, the outer seed coat (testa) has been shown to be composed of a lignin–cellulose complex (van Bergen et al., 1994a), which in monocotyledons has a significant content of *p*-coumaric and ferulic acids (van Bergen et al., 1994b). However, some taxa deviate from this, with significant amounts of proteins and tannins, and sometimes no evidence of lignin (e.g. McCobb et al., 2003). Examination of fossil seeds from a variety of taxa, depositional settings and age suggest that the lignin component of the ligno-cellulose complex in the testa is prone to be well preserved, in contrast to the cellulose component, which is often degraded during fossilisation (McCobb et al., 2001; Stankiewicz et al., 1997; van Bergen et al., 1994b; van Bergen et al., 1997a,b).

The approach in this study was to use thermally assisted hydrolysis and methylation (THM) in the

presence of tetramethylammonium hydroxide (THAH) to assess the composition of the testae (seed coat) of *Juncus* seeds buried in the top 1 m of a peat profile taken from the Faroe Islands (corresponding to ca. 900 years of peat accumulation, see below). This level of taxonomic precision reduced the effect of taxonomic variation and, combined with the high sampling resolution (1–2 cm), enabled the influence of the following factors on the chemistry of the *Juncus* testae to be assessed:

- (i) Diagenetic change after burial (i.e. with depth).
- (ii) Variation in water table depth and corresponding exposure to oxic conditions in the upper (acrotelm) layer.

Additionally, sedimentological results (Section 3.1) suggest that the site has been subject to episodic flooding from a nearby stream channel, with deposition of basaltic material (<2 mm) from the stream catchment. The lithology of the inorganic material and the depositional environment may have a significant influence on the preservation of seed coats (van Bergen et al., 1994a). The influence of the deposition of inorganic sediment on *Juncus* seed coat chemistry had therefore also been assessed. The combination of chemical data from single sub-fossil seeds of a specific taxon with the reconstruction of the local environmental setting at the time of deposition is a novel approach for examining the controls on the decomposition of organic matter in wetlands.

2. Site

Sampling was conducted on a peat bog near Masaklettur on the island of Eysturoy (6° 54.26' W, 62° 10.06' N) at an elevation of ca. 250 m a.s.l. (Fig. 1). The site is a valley mire situated close to a stream (Gjótá). The underlying geology of the bog catchment is composed of diverse basalts. The Faroes have a highly oceanic climate with a mean August temperature of 10.5 °C and mean January temperature of 3.2 °C. Precipitation ranges from 900 to 2000 mm y⁻¹ depending on position and topography (Guttesen, 1996). The site experiences relatively significant winter snow accumulation. The altitude is relatively close to the seasonal periglacial limit (ca. 100–200 m below the altitude at which patterned ground forms today; J. Hunt, personal communication).

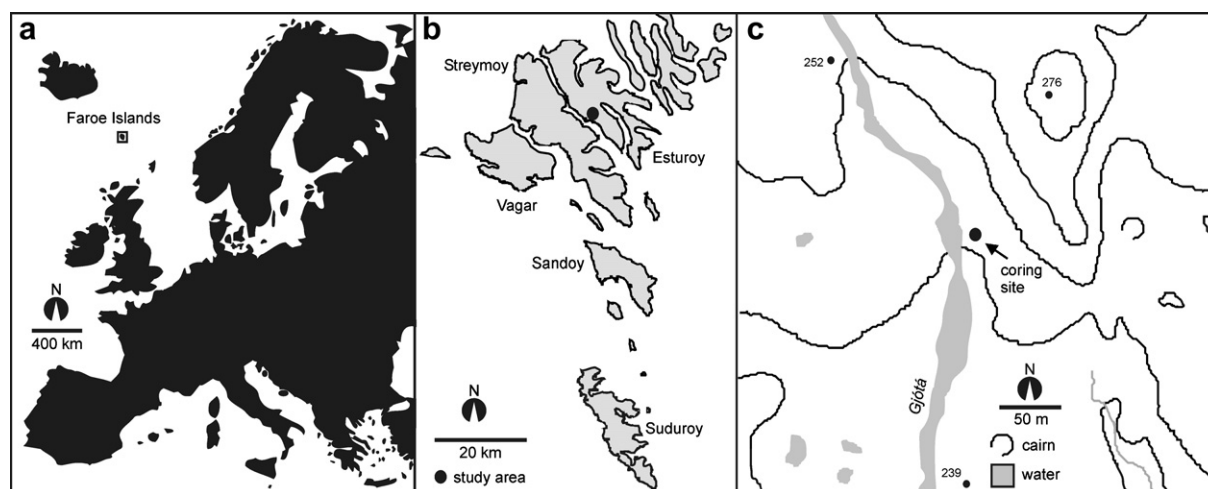


Fig. 1. Location of sampling site: (a) Europe, (b) Faroe Islands, (c) sampling site in relation to local topography (contours 10 m intervals a.s.l.).

3. Methods

3.1. Sampling and palaeoecology

Cores were collected using a monolith box for the top 50 cm and a 60 mm diameter Russian corer below this. The core was sub-sampled at contiguous 1 cm depth intervals. Radiocarbon measurements made at the Groningen radiocarbon laboratory (Table 1) show peat deposition initiated ca. 6400 cal. BC. There is a hiatus in accumulation at ca. 1 m, with an estimated end date of ca. 1030 cal. AD (M. Blaauw, personal communication). A corer of 2.6 cm diameter was used to cut macrofossil samples of ca. 5.3 cm³ from the contiguous 1 cm thick peat slices for the top 16 cm, and every 2 cm to 200 cm. These were disaggregated on a 150 µm sieve using distilled water to rinse the sub-sample. Macrofossils were scanned using a binocular microscope (×10 to ×50), and identified using an extensive reference collection of type material. Moss leaves, cyperaceous epidermal tissue and some seeds were examined at high magnification (×100 to ×400). Volume abundances of all components are expressed as percentages with the exception of *Viola* spp. seeds, *Carex* section *Paniculatae* nutlets, *Eriophorum vaginatum* spindles, *Juncus* spp. seeds, *Potentilla* spp. seeds and *Selaginella* spp. megaspores. These are presented as the number (*n*) found in each sub-sample.

Juncus seed testa from a selection of levels between 10 and 30 cm depth were mounted on permanent slides to aid identification. The testa surface

Table 1

AMS radiocarbon dates of peat profile^a

Depth (cm)	Date ¹⁴ C yr BP	GrA number	Dated material	Calibrated age 68% confidence interval
30	570 ± 50	26730	<i>Sphagnum</i> stems and <i>Juncus</i> seeds	AD 1312–1358
57	900 ± 35	26763	<i>Sphagnum</i> section	AD 1046–1093
80	1010 ± 35	26764	<i>Acutifolia</i> leaves <i>Sphagnum papillosum</i> stems, leaves and branches	AD 986–1040
94	890 ± 40	26847	<i>Sphagnum</i> stems	AD 1151–1211
101	940 ± 35	26766	<i>Sphagnum papillosum</i> stems, leaves and branches	AD 1034–1053
116	3010 ± 40	26768	Fines (<150 µm)	BC 1317–1209
116	2690 ± 50	26852	Bulk (>150 µm)	BC 857–806
			– Replicate	
140	4090 ± 45	26848	Bulk (>150 µm)	BC 2680–2573
169	5655 ± 45	26769	Bulk (>150 µm)	BC 4544–4449
			– Replicate	
169	5680 ± 45	26770	Fines (<150 µm)	BC 4553–4636
			– Replicate	
211	7470 ± 50	26849	Bulk (>150 µm)	BC 6407–6343

^a Calibration made using CALIB 5.0 (Stuiver and Reimer, 1993).

had regularly arranged punctuate thickenings on the cell wall, suggesting the seeds are of the *Juncus articulatus* type of Körber-Grohne (1964) (Fig. 2). This type includes *J. pygmaeus*, *J. anceps* *J. acutiflorus*, *J. bulbosus*, *J. articulatus* and *J. subnodulosus*.

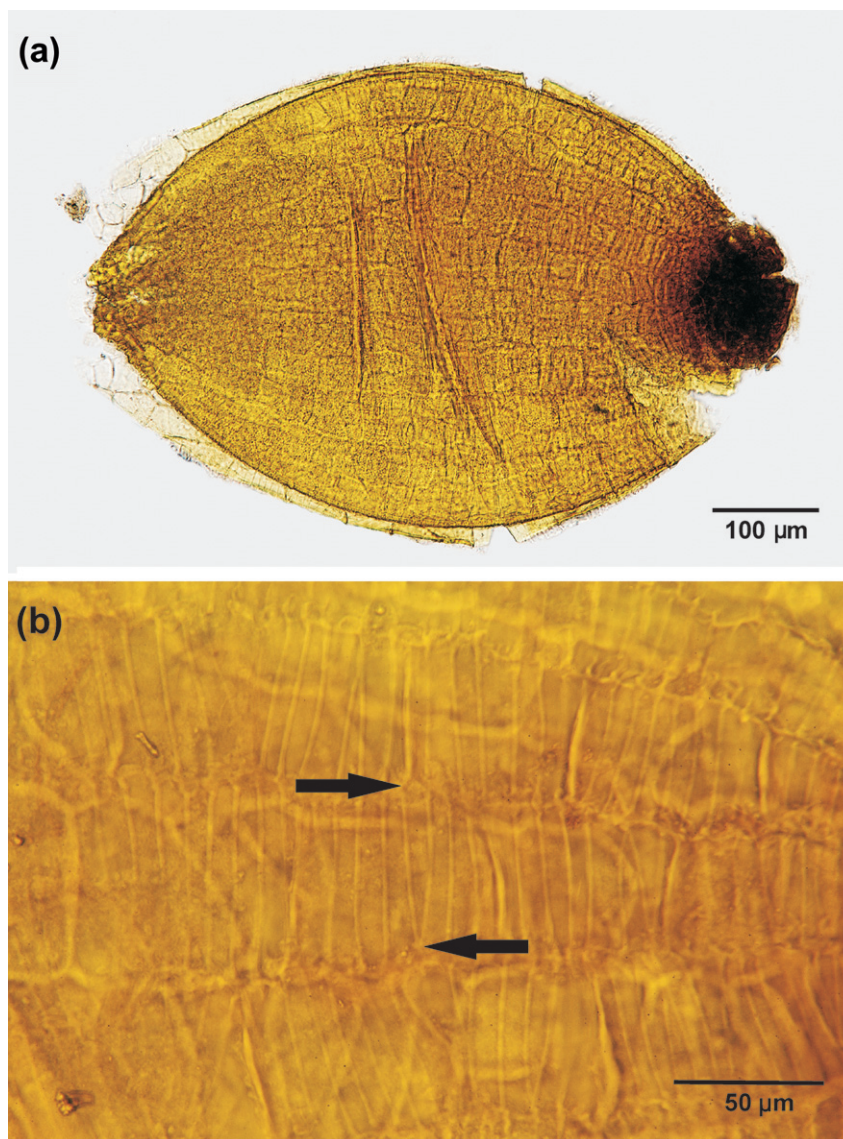


Fig. 2. Light microscope images of a sub-fossil *Juncus articulatus*-type seed (21 cm depth): (a) low magnification, (b) high magnification; arrows point to punctuate thickening on cell wall of testa (the seed was in a slightly flattened position under the coverslip).

Unfortunately, the seeds were too degraded for identification at species level. Of the *J. articulatus* seed type, *J. articulatus* and *J. bulbosus* currently occur in the same area of Eysturoy as the coring site (A.-M. Fosaa, personal communication). Juncaceae seeds have a loose seed coat. This enables an air-filled cavity to exist inside, resulting in a reduced specific weight and increased surface area. The fusi-form shape may also help keep the seed afloat longer (Werker, 1997).

To indicate the influx of basaltic material from the nearby stream channel, organic matter (OM)

content and particle size were measured. The OM content of air-dry contiguous sub-samples was determined by measuring the loss-on-ignition (LOI) at 550 °C for 4 h. The particle size distribution of the inorganic residue left after ignition was determined using a Malvern Mastersize 2000 Laser Granulometer.

3.2. Thermochemolysis

The initial approach was to characterise the chemistry of the testae of fresh *Juncus* seeds (i.e.

which had not been subject to decomposition) and identify ‘type’ compounds, representative of the major chemical groups (cellulose-related sugars, lignin-related phenolics, fatty acids). The abundance in the thermochemolysis products of the ‘type’ compounds in sub-fossil testae (the internal tissues of the seeds do not survive beyond the very early stages of decomposition) was then quantified. It should be noted that this was not an attempt to quantify original parent compounds, but to indicate the variation among pyrolysates of seed testa at different depth intervals. The emphasis was on relative changes, making quantification of the original parent compounds unnecessary. The use of a well defined sample (single testa) and TMAH as a reagent (avoiding secondary reactions) allows the reporting of results as signal of per seed.

Two *J. articulatus* seeds were collected from plants grown in the greenhouse at the Vrije Universiteit, Amsterdam on September 28th, 2005. The testae were isolated by treating the seeds with 1% HCl at 90 °C (1 h), mechanically cleaning the interior of the seeds and washing the remaining testae with demineralised water. The testae were transferred to a quartz pyrolysis tube containing a quartz filler rod (CDS Analytical Inc.), covered with 5 µL of 25% methanolic solution of TMAH; Sigma–Aldrich) and incubated (20 min) at room temperature and at 70 °C (2 h) in an oven. After incubation, the samples were heated at 700 °C (5 min) in an AS-2500 pyrolysis unit (CDS Analytical Inc.; 280 °C

interface temperature) coupled to an Agilent 6890 gas chromatograph equipped with an Agilent 5973 mass selective detector. This length of time was required to ensure complete reaction and clean the pyrolysis tube. The gas chromatograph oven was programmed from 40 °C (6 min hold) to 130 °C at 15 °C/min, to 250 °C at 8 °C/min and to 320 °C at 15 °C/min (15 min hold). A HP5-MS (30 m × 0.25 mm × 0.25) column was used, with He as carrier gas at a constant flow of 1.2 mL/min. in splitless mode. The mass spectrometer was operated in full scan mode (m/z 50–500) at 70 eV ionisation energy. Solvent delay was 6 min.

Fig. 3 shows the partial total ion current (TIC) chromatogram of the thermochemolysis products from two fresh seeds. A chromatogram from a sub-fossil seed taken from 62 depth in the peat profile is shown for comparison. Compounds were assigned on the basis of their mass spectra, applying the commercial databases Wiley 6 and NIST98. A number of compounds could not be confidently identified using these libraries. Table 2 lists six compounds recognised (Fig. 4) in the seeds, including phenolics (1, 2) and saturated (3, 4) and unsaturated fatty acid methyl esters (5) and a saccharide pyrolysis product (6). The identity of the phenolic compounds (1, 2) was confirmed using authentic standards. It should be noted that unsaturated fatty acids undergo isomerisation during THM. This results in elution of some of these unsaturated fatty acids after the saturated counterpart (Jun-Kai et al.,

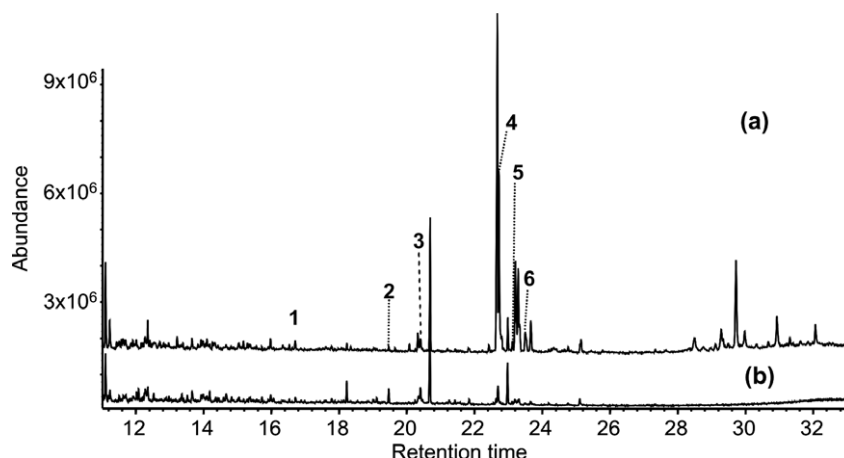


Fig. 3. Partial TIC chromatogram from thermochemolysis of (a) fresh *Juncus* testae; (b) sub-fossil seed from 62 cm depth. Numbered peaks: (1) methylated *p*-coumaric acid; (2) methylated ferulic acid; (3) hexadecanoic acid Me ester; (4) octadecanoic acid Me ester; (5) octadecadienoic acid Me ester; (6) *O*-2,3,4,6-tetra-*O*-methyl- α -D-glucopyranosyl-1,4,6-tri-*O*-methyl- β -D-fructofuranosyl, α -D-glucopyranoside.

Table 2

Specific thermochemolysis products in fresh *Juncus* seed and sub-fossil (62 cm depth) testa of *Juncus* seed

No.	Name	Compound class	Depth Decrease?	DCA1			LOI		
				r^a	p^b	$n - 1^c$	r^a	p^b	$n - 1^c$
1	<i>p</i> -Coumaric acid Me ester and Me ether	Phenol		0.063			−0.057		
2	Ferulic acid Me ester and Me ether	Phenol	Y	−0.180			−0.230^d	0.070^d	61^d
3	Hexadecanoic acid Me ester	SFAME ^e		0.139			0.041		
4	Octadecanoic acid Me ester	SFAME ^e		0.119			0.032		
5	Octadecadienoic acid Me ester	DIUSFAME ^f	Y	0.008			0.110		
6	<i>O</i> -2,3,4,6-tetra- <i>O</i> -methyl- α -D-glucopyranosyl)-1, 4,6-tri- <i>O</i> -methyl- β -D-fructofuranosyl, α -D-glucopyranoside,	Sugar	Y	−0.649^d	0.081^d	6^d	0.323		

^a Correlation coefficient (controlled for depth).^b Significance level (2-tailed).^c Degrees of freedom.^d Bold indicates $p < 0.1$.^e Saturated fatty acid methyl ester.^f Diunsaturated fatty acid methyl ester.

1997; Hardell and Nilvebrant, 1999) on an apolar column. Compound (6) is a tetramethylated glucopyranoside. Based on comparison with the mass spectra of such compounds and consideration of the MS behaviour (e.g. Tanczos et al., 2003; typical ions at m/z 101, 187 and 219 and M^{+} at m/z 292), a tentative structure is proposed (Fig. 4).

Contiguous sub-samples (1 cm sampling interval) from the top 1 m were disaggregated by gently sieving in deionised water. Sub-fossil *Juncus* seeds were hand picked under a binocular microscope. Single seeds were used for analysis. Where possible, replicate (up to three) analyses were conducted for each level. Seeds were absent from a number of depth intervals. Seeds were heated as above and the abundance of the thermochemolysates (Table 2) was quantified by integrating base peak ions.

3.3. Statistical analysis

Sub-division (zonation) of stratigraphic sequences into relatively homogeneous units enables the changes in vegetation over time to be distinguished and classified. Zonation of the macrofossil composition was conducted numerically using optimal splitting by information content (Birks and Gordon, 1985; Bennett, 1996) within psimpoll version 4.10. To explore the ecological patterns in the local vegetation composition further, detrended correspondence analysis (DCA) was conducted using the CANOCO programme (Canoco for Windows, Version 4.02). Botanic variables such as *Juncus* seeds and *Selagi-*

nella megaspores which have discrete values were not included in the analysis. Rare botanic variables and samples 28 and 68 cm were down weighted, as they appeared to be skewing the data. Rare species have great influence on correspondence analysis, and the appearance of a rare taxon for often random reasons can distort the results; statistical down weighting of rare taxa and outlying samples is therefore a standard approach in the treatment of ecological data and produces an ecological meaningful correspondence analysis where the presence of common species is emphasized.

To assess the influence of past changes in mire surface wetness and influx of inorganic material from the bog catchment on the chemistry of the *Juncus* seeds, a search for correlations between environmental and chemical variables would be problematic because the samples are in a stratigraphic sequence. They are not independent observations, and have Markovian auto-correlative properties (Birks, 1987, p.118). This problem can be solved by conducting a partial correlation. This is a biased measure of correlation between the environmental variable and the chemical response of the *Juncus* seed. The assumption is made that changes in the two variables can be represented accurately by a linear expression in depth (Gordon, 1982). Partial correlation coefficients (controlled for depth) were calculated between the environmental variables (DCA1, LOI; see Section 4.1) and the compounds listed in Table 2 using SPSS 11.0.

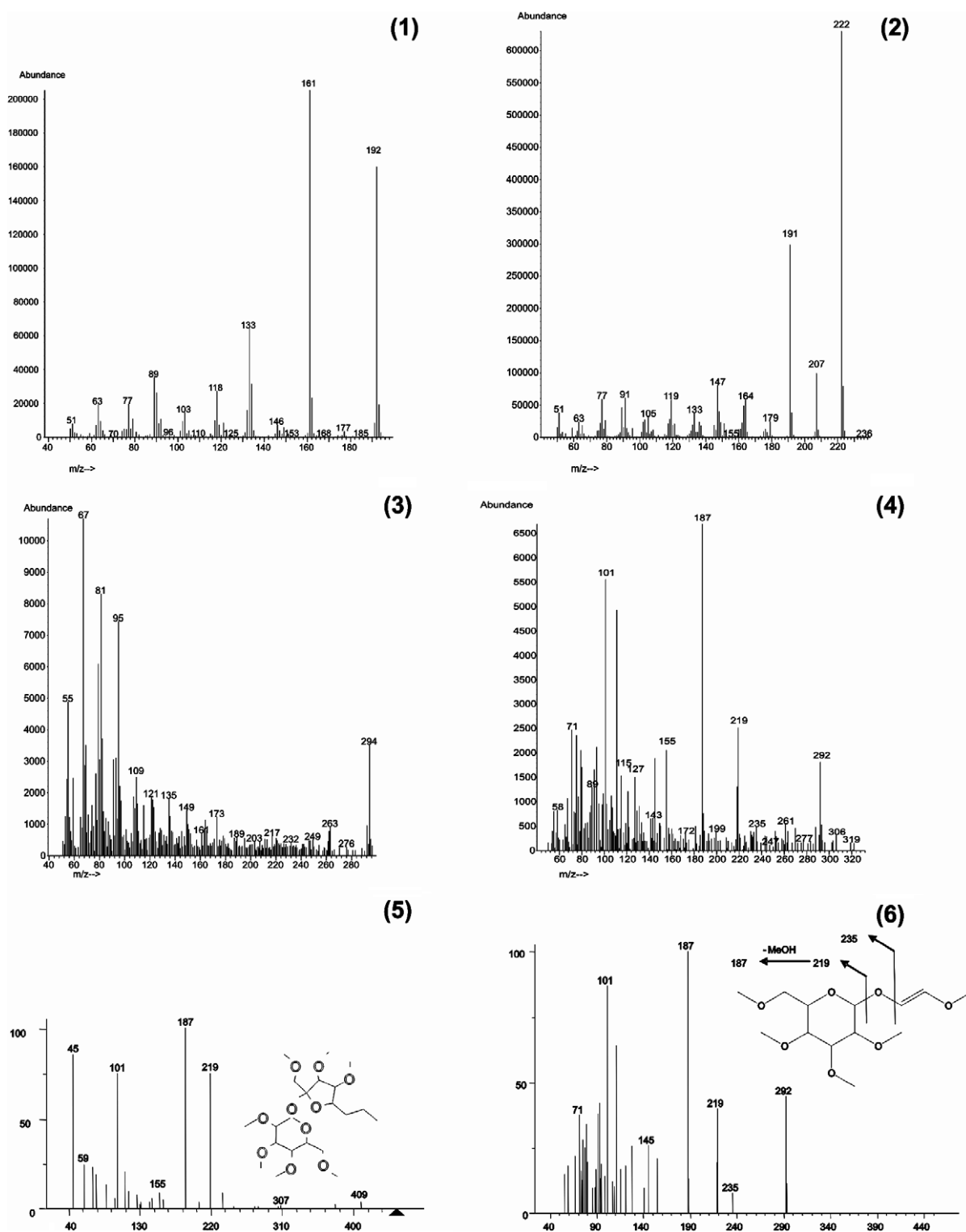


Fig. 4. Mass spectra: (1) methylated *p*-coumaric acid; (2) methylated ferulic acid; (3) octadecadienoic acid Me ester; (4) *O*-2,3,4,6-tetra-*O*-methyl- α -D-glucopyranosyl)-1,4,6-tri-*O*-methyl- β -D-fructofuranosyl, α -D-glucopyranoside; (5) NIST standard spectra for tetramethylated glucopyranoside compound (6); (6) deconvoluted spectrum (using AMDYS software) and tentative structure for (6) from interpretation of mass spectrum (M^+ , m/z 292), comparison with NIST standard spectra and MS behaviour of tetramethylated glucopyranosides (e.g. Tanczos et al., 2003).

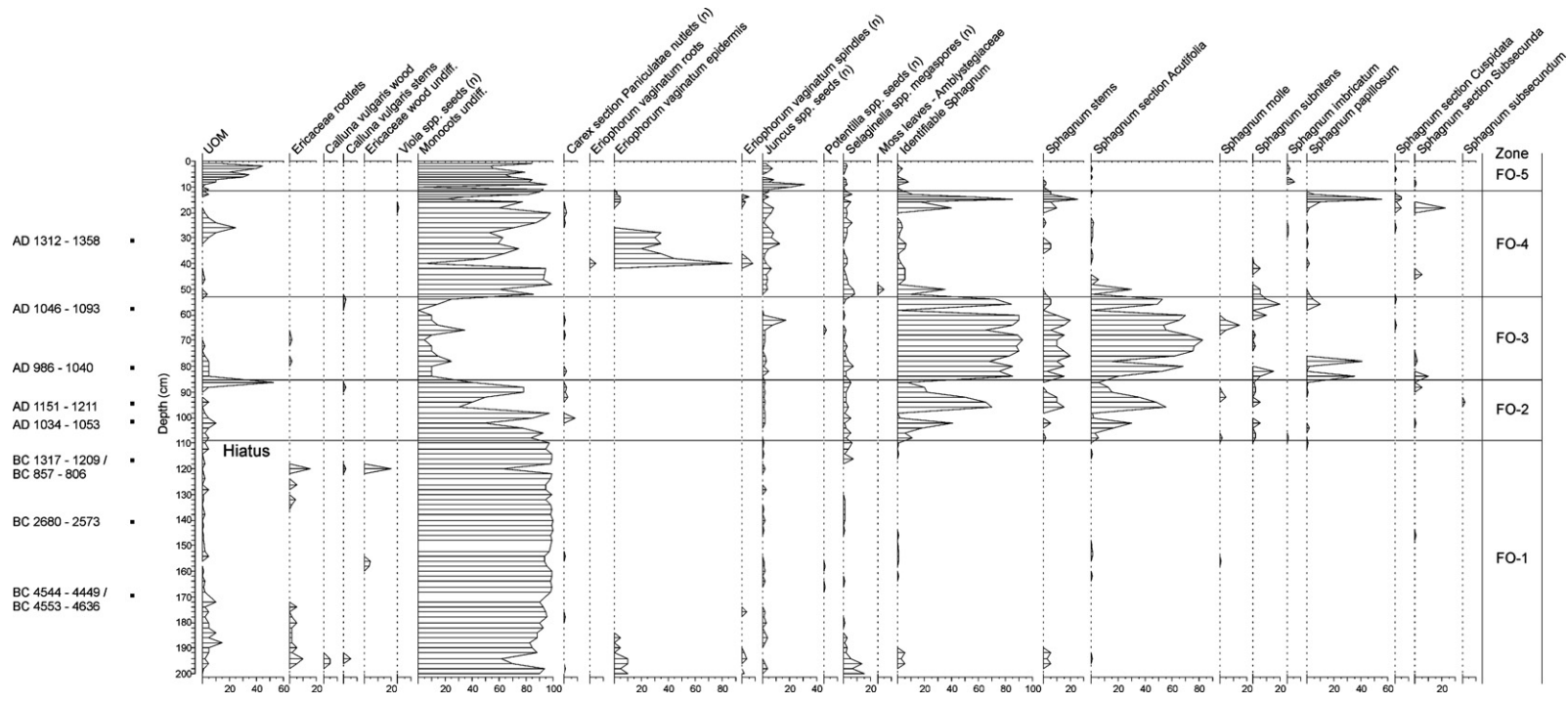


Fig. 5. Plant macrofossils. Calibrated ^{14}C age estimate (years AD/BC) stated as 1σ confidence interval. Shaded area indicates possible location of hiatus in peat accumulation.

Table 3
Plant macrofossil zone descriptions

Zone	Depth (cm)	Major Taxa	Zone description
FO-5	0–11.5	Unidentified organic material (UOM), Monocots. undifferentiated	Peat samples highly decomposed, but <i>Juncus</i> seeds and UOM record their highest values here
FO-4	11.5–53	Monocots. undifferentiated, <i>Eriophorum vaginatum</i>	Marked reduction in <i>Sphagnum</i> spp. <i>Sphagnum subnitens</i> (Russ. and Warnst.) declines, but <i>Sphagnum papillosum</i> and <i>S. s. Subsecunda</i> increase towards top of zone
FO-3	53–85	<i>Sphagnum</i> section <i>Acutifolia</i>	Consistently high values of <i>Sphagnum</i> spp. recorded, mainly represented by <i>Sphagnum</i> section <i>Acutifolia</i> . <i>S. molle</i> (Sull.), <i>S. subnitens</i> , <i>S. papillosum</i> and <i>S. s. Subsecunda</i> occur sporadically. <i>Juncus</i> seeds increase
FO-2	85–109	Monocots., <i>Sphagnum</i> section <i>Acutifolia</i>	<i>Sphagnum</i> section <i>Acutifolia</i> forms increasingly large part of sub-fossil peat matrices
FO-1	109–200	Monocots. undifferentiated	Ericales rootlets and <i>Calluna vulgaris</i> (L.) Hull. Macrofossils record their highest abundances

4. Results

4.1. Palaeoecology

The plant macrofossil diagram is presented in Fig. 5 and the main changes are listed in Table 3. The consistent presence of *Juncus* seeds throughout the stratigraphy, in addition to occasional records

of *Viola* and *Carex* seeds and *Sphagnum* section *Subsecunda* leaves, suggests the site has received slight nutrient enrichment throughout its accumulation history as a poor fen/mesotrophic bog.

The DCA results are plotted in Fig. 6. Axis 1 (DCA1) has an eigenvalue of 0.699, suggesting that it occupies the majority of the total variation in the data. One of the main factors influencing plant dis-

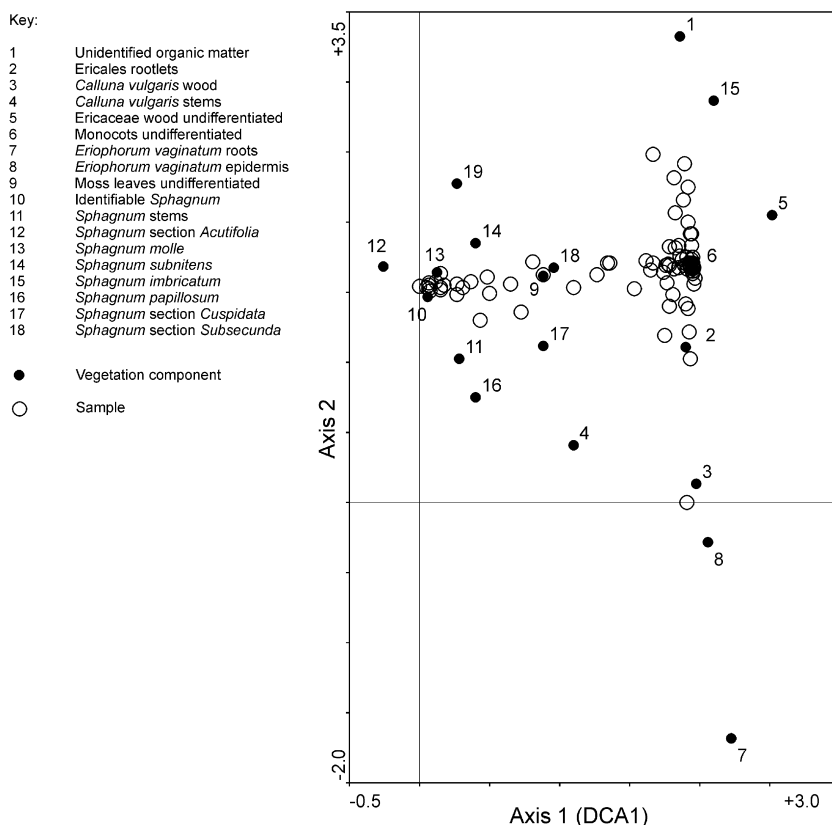


Fig. 6. Detrended correspondence analysis (DCA).

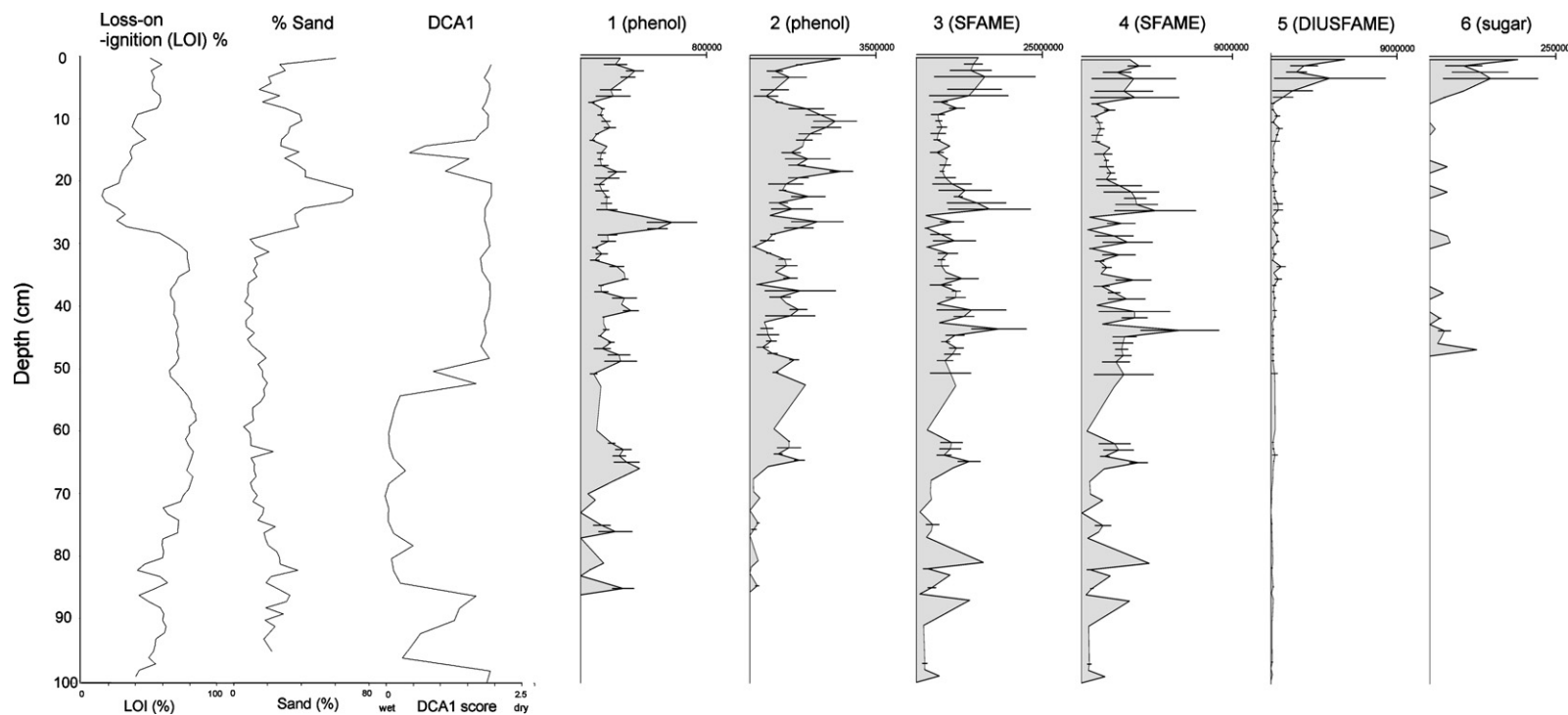


Fig. 7. Palaeoecological data (loss-on-ignition, % sand, DCA1 scores) and total ion abundances of thermochemolysis products of *Juncus* seeds. Compounds: (1) methylated *p*-coumaric acid; (2) methylated ferulic acid; (3) hexadecanoic acid Me ester; (4) octadecanoic acid Me ester; (5) octadecadienoic acid Me ester; (6) *O*-2,3,4,6-tetra-*O*-methyl- α -D-glucopyranosyl)-1,4,6-tri-*O*-methyl- β -D-fructofuranosyl, α -D-glucopyranoside. Error bars ± 1 SE. Groups: SFAME, saturated fatty acid methyl ester; DIUSFAME, diunsaturated fatty acid methyl ester.

tribution on mires is hydrology, and Axis 1 appears to indicate surface wetness. Mosses (with the exception of *Sphagnum imbricatum*, which can survive in relatively dry conditions) occupy lower values (wet), whilst monocotyledons and ericaceous plants have high DCA1 scores (dry). Plants such as *Juncus* or *Carex* need to keep their root systems away from permanently waterlogged conditions to survive.

Variation in LOI and particle size data indicate episodes of flooding from the nearby stream channel (Fig. 7). Low LOI indicates a low organic content, resulting from a large input of basaltic material from the bog catchment. A high proportion of very fine to very coarse sand size particles (62.5–2000 μm) suggests the inwashed material was deposited in higher energy, moving water conditions.

4.2. Thermochemolysis GC–MS

In addition to analytical error, some of the error in the mean estimates of abundance shown in Fig. 7 may be due to variation in the size of the seed being measured due to natural variation and/or minor physical damage such as tears and breaks.

Fig. 7 shows that the abundance of phenolic compounds (1, 2) and the saturated fatty acids (3, 4) did not decrease significantly with depth (although both phenolic compounds were not detected in testae below 85 cm). In contrast, a major loss of both the C_{18} unsaturated fatty acid (5) and the sugar (6) occurred below 7 cm in the profile. The sugar (6) did not occur in seeds below 46 cm depth.

4.3. Comparison of seed chemistry with past environmental setting

Significant partial correlation coefficients (controlled for depth) are highlighted in bold in Table 2. The sugar (6) showed a significant negative relationship (decrease in abundance in dry conditions) with the surface wetness proxy DCA1. Methylated ferulic acid (2) showed a significant negative relationship with LOI (increase with high input of inorganic material from the bog catchment).

5. Discussion

5.1. Advantages of THM over conventional pyrolysis

Pyrolysis has proved to be an especially suitable technique for the analysis of a wide variety of

biomacromolecular materials such as lignin. Furthermore, it has been used extensively for the analysis of fossil materials such as kerogen and plant fossils (Challinor, 2001). The advantage is the avoidance of laborious extraction and pretreatment procedures. This makes it especially suitable for the analysis of small samples. However, a major drawback of conventional pyrolysis techniques is the occurrence of secondary reactions, such as the recombination of pyrolysis products, decarboxylation and dehydration (Challinor, 2001). The addition of TMAH enables the avoidance of these secondary reactions and generally provides a greater sensitivity than conventional pyrolysis (Challinor, 1991, 2001). THM also enables the analysis of polymeric or macromolecular substances that are resistant to hydrolysis. No previous studies of fossil seeds have used THM (McCobb et al., 2001; Stankiewicz et al., 1997; van Bergen et al., 1994a, b; 1997a, b). For phenolic polymers such as lignin, it has been shown that the products from THM are in better agreement with the molecular structure of lignin than those from conventional pyrolysis (Challinor, 1995, 2001). The phenolics and sugar product from the *Juncus* seed coats may relate to the lignin/cellulose complex observed in previous studies (van Bergen et al., 1994a, b; Graven et al., 1996, 1997; van Bergen et al., 1997a, b; Stankiewicz et al., 1997; McCobb et al., 2001).

5.2. Diagenetic changes in *Juncus* seed coats after burial – influence of environmental setting

Major chemical changes are associated with the fresh-sub-fossil transition at ca. 7 cm depth, particularly with reductions in the C_{18} unsaturated fatty acid (5) and the sugar (6). The unsaturated fatty acid (5) may have been depleted by microbial action and oxidation, or possibly oxidative polymerisation (Versteegh et al., 2004). Our study reflects results showing that polysaccharides are rapidly degraded by fungi and bacteria in the early aerobic stages of decomposition, in contrast to the lignin-related phenolics, which are relatively well preserved (Benner et al., 1984; Kirk and Farrell, 1987; Young and Frazer, 1987; Lewis and Yamamoto, 1990; Opsahl and Benner, 1995; Akin et al., 1996; Huang et al., 1998). The rapid initial decomposition of the *Juncus* seeds concurs with mass loss estimates from short term studies of litter degradation in peat bogs during the first few years after burial (e.g. Lat-ter et al., 1998).

The mechanism by which the input of basaltic material from the nearby stream channel affected the seeds is unclear. Greater degradation would be expected in deposits subject to physical corrosion by large inorganic particles, resulting in oxidation conditions. However, in the *Juncus* seed coats, methylated ferulic acid (**2**) had relatively high abundance during periods of inundation by sand-sized particles, suggesting that the inwash of inorganic material may be responsible for the improved chemical preservation of the seeds. Mineral matrices and clay have been observed to induce the aromatization of OM during pyrolysis (Faure et al., 2006). However, in this study, this effect should not have occurred, as seed coats were isolated from the peat matrix and cleaned before pyrolysis. Diminished degradation has also been noticed for fossil seeds of Eocene deposits by van Bergen et al. (1994a, b), who suggested the following possible explanations: (i) differences in pH regime cause variation in susceptibility to biodegradation; (ii) variation in inorganic constituents influences the chemical modification of the organic material, e.g. clays with pyrite vs. sand. However, the causal mechanism for the improved chemical preservation of the seeds remains unknown.

The sugar (**6**) was easily metabolised by microbes under aerobic conditions of low water table, and preserved under anoxic conditions with high water table. The results suggest that a drier mire surface may result in the more efficient depletion of polysaccharides and cellulose during the initial stage of decomposition in the acrotelm. This may have wider implications, as the water tables of peat bogs, particularly in ombrotrophic mires, are sensitive to changes in precipitation. Peat bogs in the northern hemisphere have been estimated to contain 270–300 pG of C (Turunen, 2003) and, assuming that the bulk of the polysaccharides is metabolised to CO₂, the increased release of carbon from peatlands as dissolved OM and CO₂ resulting from a drier climate may have significant implications for the carbon cycle and feedback mechanisms within the climate system. Furthermore, this study demonstrates that the combination of palaeoecological and geochemical techniques can aid understanding of the degradation of plant material, and increase knowledge of the formation of organic deposits such as peat bogs.

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References

- Akin, D.E., Morrison III, W.H., Rigsby, L.L., Gamble, G.R., 1996. Biological delignification of plant components by the white rot fungi *Ceriporiopsis subvermispora* and *Cyathus stercoreus*. *Animal Feed Science Technology* 63, 305–321.
- Benner, R., Maccubbin, A.E., Hodson, R.E., 1984. Anaerobic biodegradation of the lignin and polysaccharide components of lignocellulose and synthetic lignin by sediment microflora. *Applied and Environmental Microbiology* 47, 998–1004.
- Bennett, K.D., 1996. Determination of the number of zones in a biostratigraphical sequence. *New Phytologist* 132, 155–170.
- Birks, H.J.B., 1987. Multivariate analysis of stratigraphic data in geology: a review. *Chemometrics and Intelligent Laboratory Systems* 2, 109–126.
- Birks, H.J.B., Gordon, A.D., 1985. *Numerical methods in Quaternary Pollen Analysis*. Academic Press, London.
- Challinor, J.M., 1991. The scope of pyrolysis methylation reactions. *Journal of Analytical and Applied Pyrolysis* 20, 15–24.
- Challinor, J.M., 1995. Characterisation of wood by pyrolysis derivatisation-gas chromatography/mass spectrometry. *Journal of Analytical and Applied Pyrolysis* 35, 93–107.
- Challinor, J.M., 2001. Review: the development and applications of thermally assisted hydrolysis and methylation reactions. *Journal of Analytical and Applied Pyrolysis* 61, 3–34.
- Clymo, R.S., 1984. The limits to peat bog growth. *Philosophical Transactions of the Royal Society of London B* 303, 605–654.
- Clymo, R.S., 1991. Peat growth. In: *Quaternary Landscapes*. University of Minnesota Press, pp. 76–112.
- Faure, P., Schleppe, L., Mansuy-Huault, L., Elie, M., Jardé, E., Pelletier, M., 2006. Aromatization of organic matter induced by the presence of clays during flash pyrolysis-gas chromatography-mass spectrometry. *Journal of Analytical and Applied Pyrolysis* 75, 1–10.
- Gordon, A.D., 1982. On measuring and modelling the relationship between two stratigraphically-recorded variables. In: *Quantitative Stratigraphic Correlation*. John Wiley and Sons Ltd., pp. 241–248.
- Graven, P., de Koster, C.G., Boon, J.J., Bouman, F., 1996. Structure and macromolecular composition of the seed coat of the Musaceae. *Annals of Botany* 77, 105–122.

- Graven, P., de Koster, C.G., Boon, J.J., Bouman, F., 1997. Functional aspects of mature seed coat of the Cannaceae. *Plant Systematics and Evolution* 205, 223–240.
- Guttesen, R., 1996. Atlas of Denmark: The Færoe Islands Topographical Atlas. Series II, Volume 5. Det Kongelige Danske Geografiske Selskab, C.A. Reitzels Forlag, København, Danmark.
- Hardell, H.-L., Nilvebrant, N.-O., 1999. A rapid method to discriminate between free and esterified fatty acids by pyrolytic methylation using tetramethylammonium acetate or hydroxide. *Journal of Analytical and Applied Pyrolysis* 52, 1–14.
- Huang, Y., Stankiewicz, A., Eglinton, G., Snape, C.E., Evans, B., Latter, P.M., Ineson, P., 1998. Monitoring biomacromolecular degradation of *Calluna vulgaris* in a 23 year field experiment using solid state ^{13}C NMR and pyrolysis GC–MS. *Soil Biology and Biochemistry* 30, 1517–1528.
- Jun-Kai, D., Wei, J., Tian-Zhi, Z., Ming, S., Xiao-Guang, Y., Chui-Chang, F., 1997. The effect of isomerization and degradation of polyunsaturated fatty acids from oils by different volume proportions of tetramethylammonium hydroxide in thermally assisted hydrolysis and methylation. *Journal of Analytical and Applied Pyrolysis* 42, 1–8.
- Kirk, T.K., Farrell, R.L., 1987. Enzymatic combustion: the microbial degradation of lignin. *Annual Review of Microbiology* 41, 465–505.
- Körber-Grohne, U., 1964. Bestimmungsschlüssel für subfossile *Juncus* samen und gramineen – früchte. *Probleme der Küstenforschung* 7, 1–47. Lax, Hildesheim.
- Kracht, O., Gleixner, G., 2000. Isotope analysis of pyrolysis products from *Sphagnum* peat and dissolved organic matter from bog water. *Organic Geochemistry* 31, 645–654.
- Kuder, T., Krüge, M.A., 1998. Preservation of biomolecules in sub-fossil plants from raised peat bogs – a potential palaeoenvironmental proxy. *Organic Geochemistry* 29, 1355–1368.
- Kuhry, P., Vitt, D.H., 1996. Fossil carbon/nitrogen ratio as a measure of peat decomposition. *Ecology* 77, 271–275.
- Latter, P.M., Howson, G., Howard, D.M., Scott, W.A., 1998. Long-term study of litter decomposition on a Pennine peat bog: which regression? *Oecologia* 113, 94–103.
- Lewis, N.G., Yamamoto, E., 1990. Lignin: occurrence, biogenesis and biodegradation. *Annual Review of Plant Physiology and Plant Molecular Biology* 41, 455–496.
- Maltby, E., Immirzi, P., 1993. Carbon dynamics in peatlands and other wetland soils: regional and global perspectives. *Chemosphere* 27, 999–1023.
- McCobb, L.M.E., Briggs, D.E.G., Evershed, R.P., Hall, A.R., Hall, R.A., 2001. Preservation of fossil seeds from a 10th century AD cess pit at Coppergate, York. *Journal of Archaeological Science* 28, 929–940.
- McCobb, L.M.E., Briggs, D.E.G., Carruthers, W.J., Evershed, R.P., 2003. Phosphatisation of seeds and roots in a Late Bronze Age deposit at Potterne, Wiltshire, UK. *Journal of Archaeological Science* 30, 1269–1281.
- Opsahl, S., Benner, R., 1995. Early diagenesis of vascular plant tissues: lignin and cutin decomposition and biogeochemical implications. *Geochimica et Cosmochimica Acta* 59, 4889–4904.
- Stankiewicz, B.A., Mastalerz, M., Krüge, M.A., van Bergen, P.F., Sadowska, A., 1997. A comparative study of modern and fossil cone scales and seeds of conifers: a geochemical approach. *New Phytologist* 135, 375–393.
- Stuiver, M., Reimer, P.J., 1993. Extended ^{14}C database and revised CALIB radiocarbon calibration program. *Radiocarbon* 35, 215–230.
- Tanczos, I., Schwarzing, C., Schmidt, H., Balla, J., 2003. THM-GC/MS analysis of model uronic acids of pectin and hemicelluloses. *Journal of Analytical and Applied Pyrolysis*, 151–162.
- Turunen, J., 2003. Past and present carbon accumulation in undisturbed boreal and subarctic mires: a review. *Suo* 54, 15–28.
- van Bergen, P.F., Collinson, M.E., Hatcher, P.G., de Leeuw, J.W., 1994a. Lithological control on the state of preservation of fossil seed coats of water plants. *Organic Geochemistry* 22, 683–702.
- van Bergen, P.F., Goni, M., Collinson, M.E., Barrie, P.J., Sinninghe Damsté, J.S., de Leeuw, J.W., 1994b. Chemical and microscopic characterisation of outer seed coats of fossil and extant water plants. *Geochimica et Cosmochimica Acta* 58, 3823–3844.
- van Bergen, P.F., Hatcher, P.G., Boon, J.J., Collinson, M.E., de Leeuw, J.W., 1997a. Macromolecular composition of the propagule wall of *Nelumbo nucifera*. *Phytochemistry* 45, 601–610.
- van Bergen, P.F., Bland, H.A., Horton, M.C., Evershed, R.P., 1997b. Chemical and morphological changes in archaeological seeds and fruits during preservation by dessication. *Geochimica et Cosmochimica Acta* 61, 1919–1930.
- van der Heijden, E., Boon, J.J., 1994. A combined pyrolysis mass spectrometric and light microscopic study of peatified *Calluna* wood isolated from raised bog peat deposits. *Organic Geochemistry* 22, 903–919.
- Versteegh, G.J.M., Blokker, P., Wood, G.D., Collinson, M.E., Sinninghe Damsté, J.S., de Leeuw, J.W., 2004. An example of oxidative polymerization of unsaturated fatty acids as a preservation pathway for dinoflagellate organic matter. *Organic Geochemistry* 35, 1129–1139.
- Werker, E., 1997. Seed Anatomy. Gebrüder Borntraeger, Berlin.
- Young, L.Y., Frazer, A.C., 1987. The fate of lignin and lignin-derived compounds in anaerobic environments. *Geomicrobiology* 5, 261–293.